

In situ transmission electron microscopy studies of silicide-mediated crystallization of amorphous silicon

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The silicide-mediated phase transformation of amorphous to crystalline silicon was observed *in situ* in the transmission electron microscope. Crystallization of nickel-implanted amorphous silicon occurred at $\sim 500^\circ\text{C}$. Nickel disilicide precipitates were observed to migrate through an amorphous Si film leaving a trail of crystalline Si. Growth occurred parallel to $\langle 111 \rangle$ directions. High resolution electron microscopy revealed an epitaxial $\text{NiSi}_2/\text{Si}(111)$ interface which was Type A. A diffusion-controlled mechanism for the enhanced crystallization rate was determined.

Thin-film metal silicides play an essential role in the increasingly fine-scale fabrication of integrated circuits.¹ The disilicides, NiSi_2 and CoSi_2 , are particularly attractive candidates for Si device fabrication due to their ability to form single-crystal epitaxial thin films with small differences in lattice parameter. Epitaxial films can be grown on clean $\text{Si}(111)$ and (100) substrates by molecular beam epitaxy and the correlation between electrical properties such as the Schottky barrier height and structural characteristics has been the subject of much research.^{2,3}

Single-crystal films of CoSi_2 have recently been produced in Si by metal ion implantation to form continuous buried layers.⁴ For Co ion doses too low to form a continuous buried layer, isolated octahedral CoSi_2 precipitates are formed.⁵ Octahedral precipitates of NiSi_2 have also been observed in wafers of Si contaminated with excess Ni.⁶ Cammarata *et al.*^{7,8} have demonstrated the formation of octahedral NiSi_2 precipitates by ion implantation of Ni into amorphous Si ($a\text{-Si}$) and investigated the kinetics of nucleation and growth. Precipitates were found to form at the peak of the implanted Ni concentration profile and the growth kinetics suggested growth of three-dimensional particles in a two-dimensional diffusion field. In addition, the silicide precipitates catalyzed formation of crystalline Si ($c\text{-Si}$).⁸ In this letter, we investigate this intriguing phenomenon of enhanced Si crystallization by employing *in situ* transmission electron microscopy (TEM) to observe dynamically the silicide-mediated crystallization of $a\text{-Si}$.

Amorphous Si thin films, 950 Å thick, were deposited by low pressure chemical vapor deposition onto 1000 Å thick thermally grown SiO_2 layers on $\text{Si}(100)$ substrates.⁹ Ion implantation of Ni into the $a\text{-Si}$ was performed at an energy of 55 keV with a dose of $5 \times 10^{15} \text{ cm}^{-2}$ to give a peak Ni concentration of $2 \times 10^{21} \text{ ions cm}^{-3}$ at a depth of approximately half the $a\text{-Si}$ film thickness. The films were annealed in a furnace at temperatures of 325–400 °C for 15 min to 3 h which allowed randomly oriented NiSi_2 precipitates to form at the peak of the Ni concentration in the

$a\text{-Si}$, as described previously.⁸ Samples were prepared for *in situ* TEM experiments by removal of the $c\text{-Si}$ substrate with chemical jet thinning in a 1:12 solution of HF:HNO₃ acid. After the *in situ* annealing, samples were removed from the TEM and single sided ion milling was performed with Ar ions at an accelerating voltage of 3 kV and 0.5 mA beam current to remove the SiO_2 layer. High resolution electron microscopy (HREM) was then carried out in a JEOL 4000EX operated at an accelerating voltage of 395 kV, with a point to point resolution of $\sim 1.8 \text{ \AA}$.

In situ TEM experiments were performed in a Philips EM430 TEM equipped with a single tilt Gatan hot stage, camera and video recorder to allow dynamic observations of the $a\text{-Si}-c\text{-Si}$ phase transformation. Experiments at 300 kV revealed a suppression of crystallization in the field of view of the TEM. Impediment of crystallization was thought to be due to knock-on displacement damage of the $a\text{-Si}$. The damage threshold for $a\text{-Si}$ is $\sim 185 \text{ keV}$. Consequently, experiments were performed at 150 keV to monitor the crystallization process. Electron beam effects were not observed under these conditions. Crystallization was found to occur in the temperature range 500–530 °C as determined by the thermocouple in the sample stage furnace. This was in good agreement with temperatures required for crystallization in a furnace. The true temperature of the TEM hot stage was not known but we estimated the measured temperature to be accurate to $\pm 30^\circ\text{C}$ by comparison with our furnace experiments and previous workers' experiments on solid phase epitaxy (SPE) of Si and SiGe in the TEM.^{9,10} The onset temperature for crystallization of Si was significantly reduced in the presence of NiSi_2 precipitates. Previous experiments on crystallization of electron-beam deposited $a\text{-Si}$ required temperatures of $\sim 700^\circ\text{C}$ for nucleation.¹¹

Precipitation of NiSi_2 was observed directly with the hot stage in the TEM. The precipitate number density was found to increase with increasing temperature, consistent with earlier observations.⁸ The crystallization of $a\text{-Si}$ was



FIG. 1. Bright-field TEM image from a partially transformed region of α -Si containing NiSi_2 precipitates and regions of crystallized Si.

mediated by the migration of NiSi_2 precipitates. Explosive crystallization of Si was not observed. Figure 1 shows a typical area of a partially transformed film heated to 500 °C. The grey background is the untransformed α -Si which contains the octahedral NiSi_2 precipitates. The film had been annealed in a furnace for 3 h at 400 °C to form the precipitates before TEM sample preparation. Regions of c -Si have been arrowed. Further insight into the crystallization mechanism was gained by monitoring individual precipitates as a function of time. Dynamic observations were recorded on video tape, but the images presented here are "snap-shots" of the process recorded on conventional TEM negatives. Figure 2 shows bright-field images of two octahedral NiSi_2 precipitates oriented in a $\langle 110 \rangle$ projection. In Fig. 2(a), which was recorded after 240 s at 507 °C, growth of c -Si has occurred on one of the $\{111\}$ faces of the lower precipitate (the white region). After 560

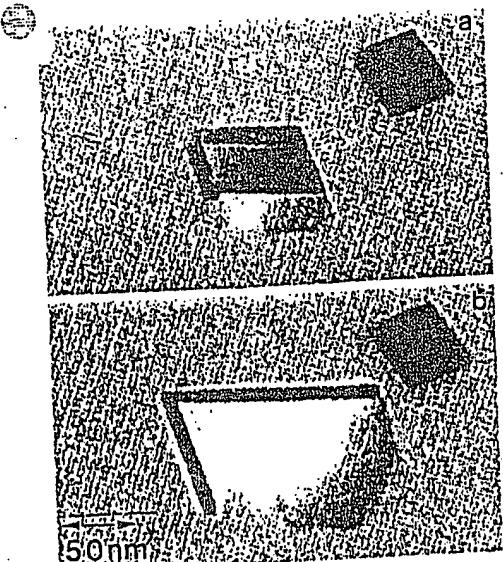


FIG. 2. Nucleation of Si on $\{111\}$ faces of octahedral NiSi_2 precipitates at 507 °C; (a) after 240 s and (b) after 560 s.

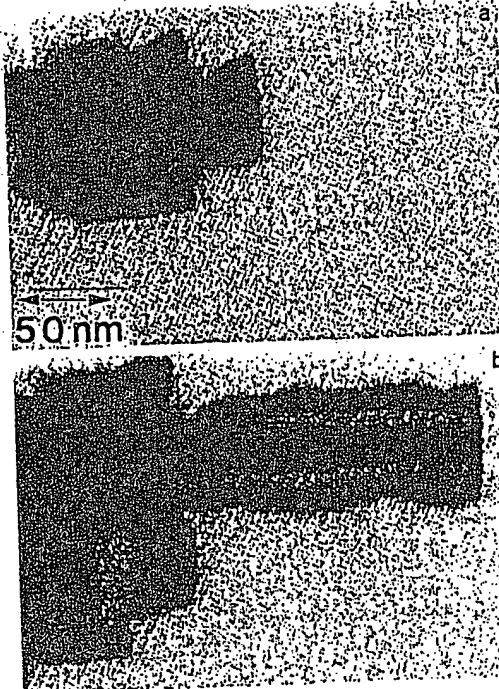


FIG. 3. Silicide-mediated growth at 507 °C; (a) after 560 s and (b) after 720 s.

s, [Fig. 2(b)] further crystallization has occurred resulting in a small region of c -Si bounded by NiSi_2 (dark bands) as shown in Fig. 2(b). Further annealing yielded large regions of c -Si, several of which showed a needlelike morphology. In films implanted with a lower Ni dose, 1×10^{15} ions cm^{-2} , the needlelike morphology was very pronounced.⁸ In the higher concentration Ni-implanted films presented here, the precipitate density was also higher and impingement with other precipitates or crystallized regions occurred rapidly. The needlelike morphology can be seen developing in Fig. 3. A partially transformed region is shown in Fig. 3(a) after 560 s at 507 °C. The Si crystal was tilted to show strong bright field contrast. After 720 s at 507 °C, [Fig. 3(b)], the needle of Si had advanced at an average velocity of $5 \pm 0.4 \text{ \AA/s}$. Following nucleation of Si at the NiSi_2 precipitates, growth always proceeded with a NiSi_2 precipitate at the planar advancing growth front. Dynamic observations revealed that the growth rate for each individual needle was dependent upon the silicide thickness in the growth direction. Many silicide particles fanned out and decreased in thickness and were observed to migrate more rapidly. A needlelike morphology developed because lateral growth of the α -Si/ c -Si interface occurred much more slowly. Growth of c -Si into α -Si is expected to occur via conventional SPE, which at these temperatures was too slow to be observed. The growth direction of the Si was parallel to $\langle 111 \rangle$ directions. This was determined by both microdiffraction and HREM analyses of the Si/ NiSi_2 interfaces.

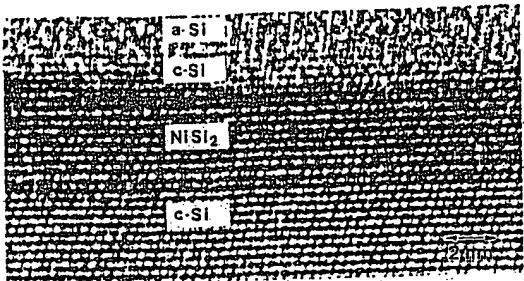


FIG. 4. HREM image of the Type A Si/NiSi₂(111) interface viewed in a [110] projection.

The annealing experiments were terminated before the films were completely transformed. The samples were removed from the TEM and additional ion milling to remove the SiO₂ layer was performed, followed by HREM examination. Figure 4 shows an example of a Si needle with a NiSi₂ precipitate at the leading edge of the c-Si. Note that a few atomic layers of c-Si appear to exist at the NiSi₂/a-Si interface. Imaging in a [110] projection allowed the (111) and (200) planes to be resolved in both the Si and NiSi₂. A flat (111) interface was found between the Si and NiSi₂ with no evidence for interfacial dislocations. The NiSi₂ precipitate in Fig. 4 is 38 Å thick. The NiSi₂ had the same orientation as the Si and the interface could thus be termed Type A. The Type B interface is more commonly observed for thin films of NiSi₂ deposited onto clean Si(111), where the NiSi₂ lattice is rotated 180° with respect to the Si substrate normal.¹² Type B interfaces were not observed after *in situ* crystallization. Solid phase epitaxy experiments on regrowth of a-Si have shown that the crystallization rates are strongly temperature dependent. Growth rates of ~8–10 Å/min have been reported for temperatures of ~550 °C for growth of (111) Si¹³ whereas in this study, Si growth at ~5 Å/s occurred for temperatures of ~500 °C. Our experiments suggest a significant enhancement of the growth rate of Si with the addition of Ni to a-Si compared to SPE.

Enhancement of Si crystallization due to the presence of a silicide layer has previously been reported for SPE of Si through, for example, palladium silicide layers¹⁴ and for Ni deposition on hydrogenated a-Si.¹⁵ The metal silicide plays a crucial role in aiding the a-Si to c-Si phase transformation. Nygren *et al.* have reported the rapid crystallization of In-implanted a-Si by the migration of droplets of liquid In.¹⁶ In the experiments described here, crystallization of a-Si occurred via the migration of solid phase NiSi₂ precipitates. The earliest stage of the a-Si–c-Si transformation appeared to involve the formation of a few atomic

layers of c-Si on one or more of the [111] faces of the octahedral NiSi₂ precipitates. An interaction occurred between the metallic silicide and the Si that facilitated the crystallization of Si. The very small difference in lattice parameter that exists between the c-Si and NiSi₂ (0.4% at room temperature), enabled the formation of epitaxial c-Si. In the direction of precipitate motion, Ni diffused into the c-Si from the precipitate, forming new silicide. Diffusion of Ni toward the growing interface from the rear of the precipitate took place, leaving epitaxial c-Si. As the precipitate advanced, crystallization of Si occurred again at the new silicide/a-Si interface and repetition of this process resulted in the migration of precipitates leaving trails of c-Si. If it is assumed that the process is diffusion limited, then it is expected that the velocity, V , of a migrating precipitate should vary as $V = D/t$, where D is a kinetic parameter which can be taken as an effective diffusivity and t is the thickness of a precipitate. The observation of an increasing crystallization rate with decreasing precipitate thickness strongly suggested that the transformation kinetics were controlled by diffusion through the silicide rather than by an interface reaction. We acknowledge valuable discussions with David A. Smith and Frans Spaepen and the contributions of S. F. Nelson, C. V. Thompson, and K. N. Tu.

- ¹K. N. Tu, in *Advances in Electronic Materials*, edited by B. Wessels and G. V. Chin (American Society for Metals, Metals Park, OH, 1986), p. 147.
- ²R. T. Tung, Phys. Rev. Lett. 52, 461 (1984).
- ³M. Liehr, P. E. Schmidt, F. K. LeGoues, and P. S. Ho, Phys. Rev. Lett. 54, 2139 (1985).
- ⁴A. E. White, K. T. Short, R. C. Dynes, J. P. Gorno, and J. M. Gibson, Appl. Phys. Lett. 50, 95 (1987).
- ⁵C. W. T. Bulle-Lieuwma, A. H. van Ommen, and L. J. van Ijzendoorn, Appl. Phys. Lett. 54, 244 (1989).
- ⁶P. D. Augustus, Inst. Phys. Conf. Ser. 67, 229 (1983).
- ⁷R. C. Cammarata, C. V. Thompson, and K. N. Tu, Appl. Phys. Lett. 51, 1108 (1987).
- ⁸R. C. Cammarata, C. V. Thompson, C. Hayzelden, and K. N. Tu, J. Mater. Res. 5, 2133 (1990).
- ⁹D. C. Paine, D. J. Howard, N. G. Stoffel, and J. A. Horton, J. Mater. Res. 5, 1023 (1990).
- ¹⁰R. Hull, J. C. Bean, D. J. Eaglesham, J. M. Bonar, and C. Buescher, Thin Solid Films 183, 117 (1989).
- ¹¹J. L. Batstone, Bull. Am. Phys. Soc. 36, 577 (1991).
- ¹²R. T. Tung, J. M. Gibson, and J. M. Poate, Phys. Rev. Lett. 50, 429 (1983).
- ¹³L. Csepregi, E. F. Kennedy, T. J. Gallagher, and J. W. Mayer, J. Appl. Phys. 48, 4234 (1977).
- ¹⁴S. S. Lau and W. F. van der Weg, in *Thin Films–Interdiffusion and Reactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1978), p. 450.
- ¹⁵Y. Kawazu, H. Kudo, S. Onari, and T. Arai, Jpn. J. Appl. Phys. 29, 2698 (1990).
- ¹⁶E. Nygren, J. C. McCallum, R. Thornton, J. S. Williams, and G. L. Olson, Mater. Res. Soc. Symp. Proc. 100, 405 (1988).